Synthesis, Characterization and Optical Properties of CaF_2 and Pb Doped CaF_2 Nanocrystals

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***Abstract*: Calcium Fluoride and Lead (Pb) doped Calcium Fluoride (CaF_2) nanocrystals were synthesized by the co-precipitation method and characterized by powder X-ray diffraction (PXRD) as well as Scanning Electron Microscopy (SEM). Optical absorption (UV-Visible) and photoluminescence (PL) studies were carried out. The PXRD patterns show cubic structure of the synthesized nanocrystals. The morphological features studied by SEM revealed that nanocrystals were agglomerated but porous. The optical absorption spectrum gave a strong and prominent absorption peak at 235 nm. Energy band gap of 4.6 eV for Pb doped $CaF_2$was calculated using Tauc's plot from the optical absorption spectra. The energy band gap is higher for doped CaF_2 as compared to pure CaF_2 nanocrystals (2.9 eV) and increases with the doping content. The PL spectrum gives broad band emission at 345 nm along with a small but distinct emission at 482 nm.**

Keywords: Nanocrystals, co-precipitation, optical properties, absorbance, energy band gap, luminescence.

INTRODUCTION

The structural, magnetic, optical, dielectric, thermal and other physical properties of materials in the nanometer domain are different from those of bulk materials due to their large surface area to volume ratio and quantum confinement effects [1]. Fluoride compounds are very attractive materials for many potential applications such as phosphors, photonics, display monitors, imaging, light amplification and precursors for transparent ceramic processing [2]. Among the alkali fluoride compounds, Calcium Fluoride CaF_2 is an attractive material because of its high stability and non-hygroscopic behavior. CaF_2 is a well known host for luminescent ions due to its high transparency in a broad wavelength range, low refractive index and low phonon energy. CaF_2 is one of the fluorides with wide band gap and has a large scale transparency [3]. Recently, CaF_2 has gained much interest as a laser material when doped with rare earth materials [4]. In references to previous work on the fluorides, it was observed that the properties of the material can be tuned by the doping of metals. However, the reports on synthesis of Pb-doped CaF_2 nanocrystals are very rare.

EXPERIMENTAL

Synthesis of CaF_2 and Pb doped CaF_2 nanocrystals

In the present work, pure CaF_2 nanocrystals and Pb (3 mol %) doped CaF_2 nanocrystals were synthesized by co-precipitation method.

For synthesis of CaF_2, stoichiometric quantities of $CaCl_2.6H_2O$ and NH_4F and were taken in a 250 ml beaker and dissolved in 100 ml distilled water. The mixture was stirred for 3 hours constantly to achieve homogeneity. During stirring, the transparent reaction mixture transforms into opaque white suspension gradually. After stirring for 3 hrs, the solution was centrifuged with ethanol for 15 min at 3000 rpm. White residue was obtained. The residue was washed thoroughly with absolute ethanol to remove the residual chloride and the ammonium ions, taken on a Petri dish and dried at room temperature. The final product was white powder. The Pb (3 mol %) doped CaF_2 nanocrystals were synthesized using the same process.

Characterization

The XRD measurement was carried out using a X'Pert Pro PANalytical powder diffractometer with Cu-Kα radiation (λ = 1.54060 Å) in the scan range 20-90º. The morphology of synthesized sample was studied using scanning electron microscopy on a machine of JEOL make MODEL JSM 5810 LV. The optical absorption spectrum was carried out on a Thermo Scientific Evolution 600 UV-Visible spectrometer in a range 200-900 nm. For UV-Visible characterization the sample was dissolved in absolute ethanol and the absorbance was taken as a function of wavelength. The PL spectrum was carried out on a JASCO 6300 spectrophotometer.

RESULT AND DISCUSSION

Powder X-ray diffraction (XRD) analysis

Figures 1(a) and 1(b) show the PXRD pattern of as-synthesized CaF_2 and Pb-doped CaF_2 nanocrystals. All the obtained diffraction peaks were indexed and assigned

to a cubic phase of the fluorite type structure with space group Fm3m. The pattern was compared with JCPDS card no. 77-2245 and 75-0363. The diffraction patterns confirm the cubic structure of the synthesized nanocrystals. The displayed peaks correspond to (hkl) values (111), (200), (220), (311), (400), (331) and (422). The lattice constant (*a*) was calculated by using (hkl) values. The average value of lattice constant was found to be 5.4739 Å for Pb doped CaF_2 and 5.46868 Å for undoped CaF_2 sample. This small difference may be due to the fact that when Ca^{+2} is substituted by a Pb^{+2} ion, charge compensating F^- ions enter the Fluorite (CaF_2) structure in interstitial cubic sites and the electronic repulsion between F^- ions leads to a net increase of the lattice parameter.

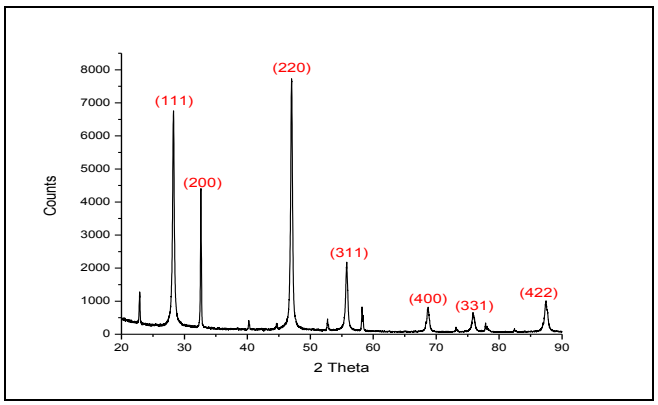


Figure 1(a): PXRD of CaF_2 nanocrystals

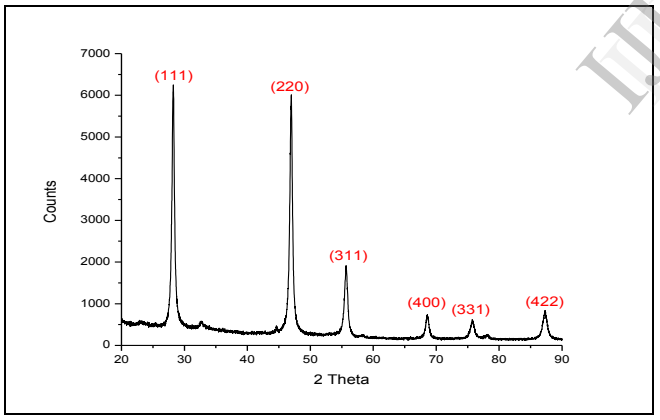
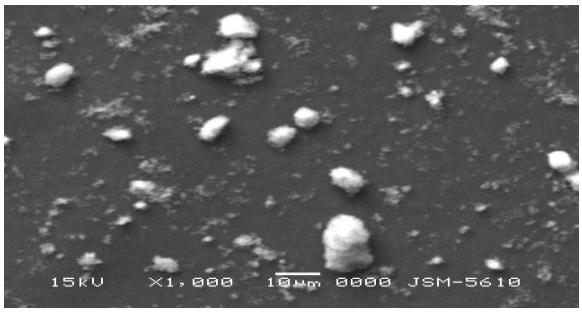


Figure 1(b): PXRD of Pb doped CaF_2 nanocrystals

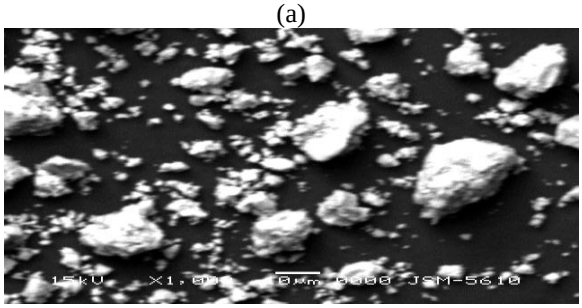
The crystallite size was calculated by Scherer's formula. It was found to be 53 nm for CaF_2 and 21.4 nm for Pb doped CaF_2. It is observed that the crystallite size of CaF_2 decreases when doped with Pb.

SEM analysis

Figure 2(a) and 2(b) shows a SEM image of as-prepared CaF_2 and Pb doped CaF_2 samples. The SEM image reveals the morphology of the synthesized nanocrystals. The CaF_2 nanocrystals are agglomerated, fluffy but porous. The agglomeration ranges from few microns to tens of microns.



(a)



(b)

Figure 2: SEM image of (a) CaF_2 and (b) Pb doped CaF_2 nanocrystals.

Optical absorption

Figure 3 shows the optical absorption spectrum of CaF_2 and Pb-doped CaF_2 nanocrystals. The absorption spectrum shows that characteristic absorption peak is present in the UV-region and also shows that by doping of the Pb, absorbance increases as compared to pure CaF_2 nanocrystals. The prominent absorption peak observed in Pb doped CaF_2 is at 235 nm.

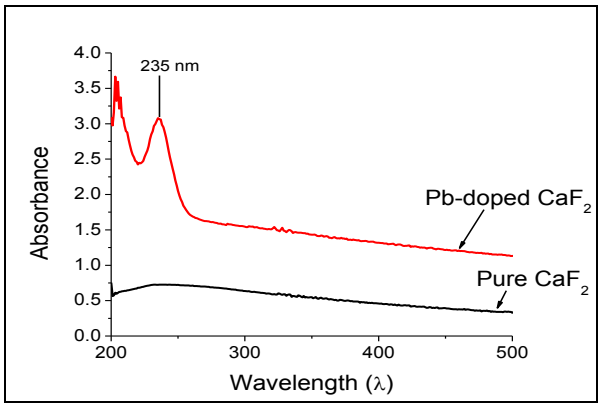


Figure 3: optical absorption spectrum of CaF_2 and Pb-doped CaF_2 nanocrystals

The energy band gap E_g was obtained from the optical absorption spectra by extrapolating the straight line plot of $(\alpha h\nu)^2$ versus $(h\nu)$ to the energy axis by the method proposed by Wood and Tauc [5]. It was found to be 2.9 eV (Figure 4(a)) for CaF_2 and 4.6 eV (Figure 4(b)) for Pb-doped CaF_2 nanocrystals. It is observed that doping of the Lead (Pb) ions in CaF_2 tends to change the energy band gap of the material.

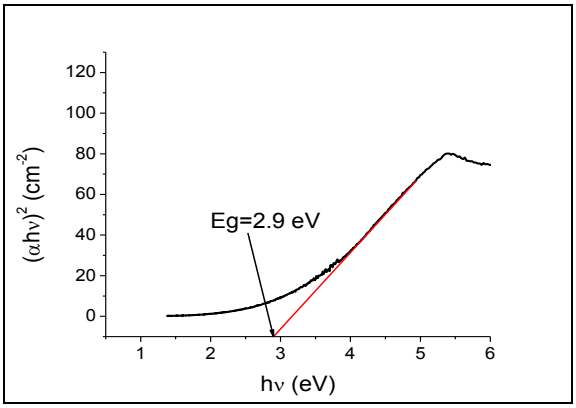


Figure 4(a): Energy band gap plot of pure CaF_2 nanocrystals.

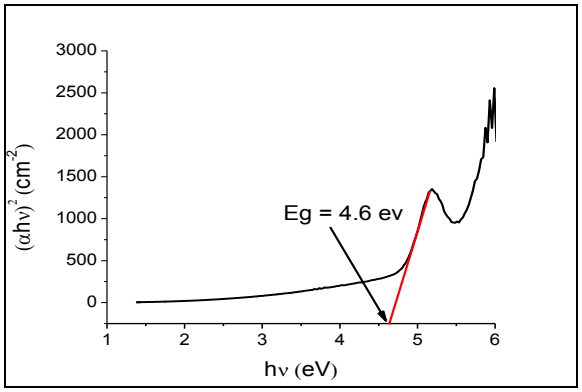


Figure 4(b): Energy band gap plot of CaF_2: Pb nanocrystals.

Photoluminescence

Figure 5 shows the PL emission spectrum of pure and Pb-doped CaF_2 for excitation at 235 nm.

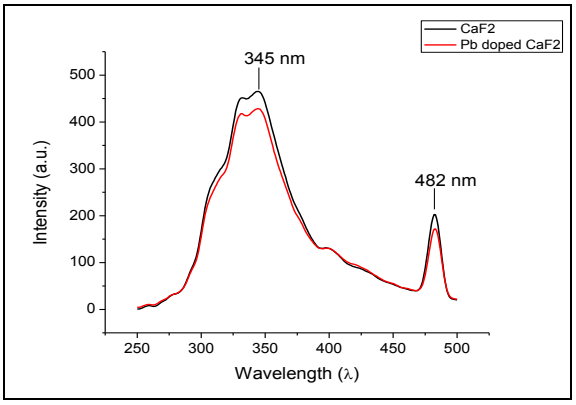


Figure 5: PL emission spectrum of CaF_2 and Pb-doped CaF_2 nanocrystals excited at 235 nm.

Broad emission was observed at 345 nm along with a small but distinct emission peak at 482 nm, when the sample was excited at 235 nm. Pb-doped CaF_2 nanocrystals show luminescence of pure CaF_2 with a small decrease in intensity of the emission peak [6]. Both the pure as well as doped samples show exactly the same spectral characteristics. Hence, the emission can be attributed to the host lattice. The difference in intensity between the emission peaks may be either due to doping or due to different amounts of sample taken for measurement.

CONCLUSIONS

In summary, synthesis technique, co-precipitation was employed to make CaF_2 and Pb-doped CaF_2 nanocrystals. XRD measurement indicates that a cubic crystalline phase can be obtained on a nanometer scale. SEM result revealed that the nanocrystals were agglomerated but porous. The optical absorption spectrum showed a strong and prominent peak at 235 nm and it is observed that the energy band gap of CaF_2 nanocrystals increases by doping of Pb ions. Photoluminescence spectra showed a broad emission at 345 nm with a blue emission peak at 482 nm.

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